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The unit developed is capable of meeting or exceeding the design criteria originally specified. The mean air velocity was 0.34 m sec^{-1} which is consistent with Taylor's recommendation of slightly less than 0.5 m sec^{-1} . The light intensity as measured by the photon flux density exceeded $300 \mu\text{E m}^{-2} \text{ sec}^{-1}$ for new fluorescent tubes and it declined to $275 \mu\text{E m}^{-2} \text{ sec}^{-1}$ when the tubes were fully aged. Thus as the physical performance of the unit is comparable to the performance of commercial units, its economy of construction offers considerable financial savings for research programmes requiring extensive controlled environment facilities.

We have not detailed the precise production costs because these will vary between countries. However, on the basis of our records of the total financial outlay on the project, the materials cost per cabinet was only 25 per cent of a locally manufactured commercial cabinet of a similar size. Thus even after a generous allowance for labour at a value equivalent to the materials, a saving in equipment costs of 50 per cent should be possible. The design is well suited to construction by a skilled carpenter and it requires only minimum of labour from electrical and refrigeration tradesmen. An equipment list and constructional notes are available from the authors.

Acknowledgments

We wish to acknowledge the skilled work of our laboratory craftsman, Mr. R. B. Brandschied, in developing the construction techniques and building the units. Mr. B. Gibbs, CSIRO, Buildings Branch, gave valuable assistance with the original design, and Mr. G. R. Nicol of our laboratory assisted with the development of the electronic temperature control units.

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Measuring CO₂ in air using glass sample tubes and GC

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Abstract

A simple system for measuring CO₂ in air using glass sample tubes fitted with Butyl rubber Suba-seal stoppers is described. A 1 ml aliquot is taken from the tube and is injected directly onto a gas chromatograph. The sample tubes and stoppers were adequately leak proof to CO₂ and can be sent through the post to a central testing laboratory. The system has applications in agriculture and air conditioning studies and was used to measure the CO₂ level in the air in glasshouses, a poultry unit, a conference room, an aircraft, and in other locations.

THERE are a number of situations where it is necessary/desirable to measure the CO₂ level in air, viz.

Enrichment situations

As in the case of early season production of tomatoes under glass with a CO₂ level of 1000 p.p.m. is desirable to enhance growth.

Build-up situations

- in air change studies where CO₂ builds up in a room or vehicle in which there are people, or in the case of build-up in intensive poultry or pig units.
- where CO₂ is produced by fermentation, as in a brewery, or by respiration of fruit and vegetables in a storage room or storage pack.
- where CO₂ is a product of combustion, i.e. the presence of above atmospheric levels of CO₂ may be an indication of the leakage of flue gases in heating systems.
- in more complex systems such as the build up of CO₂ in the air in soil.

There are many other situations not mentioned above where it also may be necessary to measure CO₂.

On-site and off-site CO₂ measurements

The measurement of CO₂ can take place on-site using many techniques, e.g., colourmetric CO₂ tubes, Orsat apparatus, conductivity measurements, in-line gas chromatography, I.R. analyzers and other methods. However, in many cases it is not feasible or convenient to carry out the measurement on-site and samples must be brought to a laboratory for analysis.

This paper reports a simple system for off-site CO₂ measurements which utilizes small glass sample tubes with Suba-seal stoppers at both ends for taking and holding the samples and a gas chromatograph for the actual measurement. The aliquot to

be measured is removed with a hypodermic syringe from the sample tube and is injected directly into the gas chromatograph.

Sample tubes and stoppers

The sample tubes used were glass, 1.4 mm wall thickness, with i.d. 27.2 mm and 152 mm long. Each tube was fitted with a No. 57 Butyl rubber Suba-seal stopper at both ends. The stoppers were pushed fully home and were then overlapped over the glass.

Tests on different methods of filling these tubes with the air sample were carried out in a glasshouse in which the atmosphere was enriched with CO₂. The tubes had been previously flushed with outside fresh air, which contains $0.033 \pm 0.001\%$ CO₂ (Handbook of Chemistry and Physics), and the stoppers inserted. The filling methods tested were:

- pushing a cotton wool plug through the tube to displace the air in the tube.
- waving the tubes in the air at full arms length through a 90° arc, 10, 20 or 50 times.
- leaving the tubes on a table in the glasshouse for 1, 2 and 4 min.

The different filling methods gave similar results. However, for practical purposes, the technique of pushing a cotton wool plug through the tubes was found most suitable and was used for all subsequent tests. Care must also be taken to allow the tube to warm up to glasshouse temperature before removing the stoppers to permit entry of the sample. Otherwise, condensation will form on the inside of the tube which may dissolve CO₂ and give a falsely high reading.

Tests were also done using thick-walled polythene tubes instead of glass ones. However, these were found unsatisfactory due to leakage of CO₂. Polythene tubes which contained a high level of CO₂ seemed to soak-up some of it and then release it over a period of time.

The sample containers (tube and stoppers) were tested for leaks by injecting CO₂ with a hypodermic syringe into the tubes and then following the CO₂ levels over a period of time. Every tube was fitted with two Suba-seal stoppers each of which had been pierced 0, 25, 50, 75 or 100 times with a hypodermic syringe to study how many times a set of two stoppers could be used before they began to leak. One stopper in each tube was pierced an additional 5 times, once to inject the CO₂ into the tube, and 4 further times over a period of 10 days to remove samples to test the CO₂ content.

The results (Table I) show that tubes fitted with stoppers pierced up to 25 times were reasonably CO₂ proof for 10 days and would be suitable for the type of measurements for which the system was designed, i.e., where a reading within $\pm 5\%$ of the actual value would be adequate. A system of one tube and two stoppers could be used, 50 times, therefore, i.e. 25 punctures in each stopper. It would also be necessary to number each stopper and record how often it had been pierced.

Stoppers pierced >25 times would only be suitable in sample tubes where the sample was measured the same day as it was taken. If very precise results are required it would be necessary to use stoppers that were not previously pierced and also to ensure that they fitted the glass tube tightly. Particular care would also need to be taken that the stopper was fully overlapped on the glass.

If the sample tube contains a very high level of CO₂ then it is desirable to use unpierced stoppers as even a tiny hole will result in significant leakage. In a test using unpierced stoppers, a sample tube that contained air with a CO₂ content of 40,833 p.p.m. on day 0 had 38,739 p.p.m. after 5 days, a loss of just over 5%. However, it is unlikely that levels as high as these would be encountered frequently in practice. In instances where they did occur, a dilution could be prepared by injecting a sample rather than filling the whole tube with the atmosphere.

Gas chromatography measurements

Samples (1 ml) were withdrawn from the sample tubes with a Becton and Dickinson plastic medical syringe fitted with a blue coded needle numbered 23g $\frac{1}{4}$, 30/6, N $\frac{1}{4}$ 14 and were injected directly into an F17 Perkin Elmer gas chromatograph. Silica gel (60–80 mesh) columns 2 m long and 3 mm i.d. were used. The hot wire injector block was at 150°C, the oven at 125°C and the filament at 300°C. The carrier gas was He with a flow rate of about 40 ml/min. A supply of N₂ was attached to the He line to enable the system to be conditioned with N₂ while only switching to He, which is much more expensive, for the actual analysis. The retention time for the CO₂ was 1.5–2 min and the CO₂ peak was followed by a broad positive and a broad negative peak which was caused by the direct injection technique. A sample could be injected every five minutes giving a total of 12 samples per hour. The baseline drift over this period was 4 mm.

The precision of the system was tested using two sets of duplicate samples and the variables sampling equation (Kramer and Twigg, 1966):

$$n = \left(\frac{ks}{e} \right)^2$$

where n = number of samples for a result of a desired precision

where k = number of standard deviations

where e = desired precision, i.e. percentage on each side of the mean.

A value of $\pm 5\%$ was chosen for e and 1.65 (90% assurance) for k . The value for s was calculated from the tests on duplicates and the number of samples (n) that needed to be tested to ensure that the result would not be more than $\pm 5\%$ from the mean 90% of the time was obtained. In the first test 10 replicate 1 ml samples were removed from a sample tube into which a small portion of pure CO₂ had been injected. In the second test 10 replicates were removed from a sample tube that contained outside fresh air. The values for n were less than 1 (Table II) which indicated that it was necessary to test only one sample from the sample tube to get a result within the required precision limits. This showed that the syringe, the method of removing the sample from the tube, the injection technique, and the performance of the column and detector were all satisfactory.

The temperature of the gas in the sample tube had little effect on the CO₂ level obtained. A standard sample which was stored for 12 hr at each of the temperatures 0, 21, 27°C had corresponding CO₂ levels of 2210, 2245 and 2188 p.p.m. respectively.

Preparation of CO₂ standards

Carbon dioxide standards for calibrating the gas chromatograph were prepared by injecting known amounts of pure CO₂ into narrow necked 1 litre volumetric flasks fitted with No. 29 Butyl rubber Suba-seal stoppers. The total volume of each flask was measured by filling to the top with water. The flask was dried and flushed with N₂ to remove all air. The stopper was inserted as the N₂ flushing tube was removed and a 1 ml sample was removed and injected into the gas chromatograph to prove absence of CO₂. Pure CO₂ was then injected into the flask; for example 1 ml of pure CO₂ in a flask of total volume 1020 ml makes a standard of 980 p.p.m. CO₂. It is important to allow the pure CO₂ to diffuse in the volumetric flask for 12 hr to ensure that it is uniformly mixed with the N₂. Standards prepared in this fashion were checked against fresh air and were found satisfactory. No leakage of CO₂ occurred through the small No. 29 Suba-seal stoppers and such standards could be used at least 40 times.

Practical use of the CO₂ measuring system

The main advantage of this system lies in the sample tubes. These are robust and leak proof (within the limits required), compared to balloons and plastic bags, and can be sent through the post to a central testing laboratory. They can be used to take samples directly as described above, or alternatively, sub-samples from atmospheres or other containers can be injected into them. The fact that a set of two stoppers can be used 50 times is advantageous.

One of the main applications envisaged for the above system is to provide a service for CO₂ monitoring in glasshouses during the period December–March when enrichment is carried out using

Table I Carbon dioxide levels (ppm) in tubes fitted with Suba-seal stoppers pierced different numbers of times with a hypodermic syringe.

Number of punctures	Time (days)			
	0	2	5	10
0	3095	3038	3082	2963
25	2583	2552	2426	2513
50	2610	2563	2580	2481
75	3576	3270	3200	2919
100	3107	2579	2401	1949

Table II Number of samples to be tested per sample tube for a result of a desired precision*

Number of duplicates	Mean CO ₂ content (ppm)	SD	Number of samples to be tested (n)
10	1494	35.60	0.62
10	330	3.25	0.11

*a precision value of $\pm 5\%$ was chosen.

Table III Carbon dioxide levels (ppm) in air from different locations.

Location	Comments	CO ₂ content
Pre-fab school room	50 infants	2590
BAC 1-11 jet – full	Sampled $\frac{1}{4}$ hr after take-off	2254
BAC 1-11 jet – $\frac{1}{2}$ full		1666
Tennis club		4786
Conference Centre	Air conditioned, 80 people	700
Bridge (cards) room	64 people	2211
Poultry farm,	room (a) – 4 fans working	1060
3000 birds/room		room (b) – 3 fans working
Flue gases in air-heated glasshouse	Fan on, burner off	418
	Fan on, burner on	1145

bulk CO₂ or by burning propane. Growers and advisers will be issued with tubes and stoppers and they will send samples, in a similar fashion to soil samples, for testing.

In preliminary tests in glasshouses, wide variations on each side of the optimum figure of 1000 p.p.m. CO₂ were found, with values as high as 3357 p.p.m. and as low as 168 p.p.m. The latter value indicates that the tomato plants were using CO₂ at a faster rate than it was being supplied, and that the glasshouse was reasonably air-tight. Air tightness tests can be carried out in glasshouses with this system and in one example CO₂ levels of 300, 350 and 583 p.p.m. were found in the southwest, middle and northeast parts of a glasshouse ($\frac{1}{4}$ acre in size) respectively, on a day in which a strong southwest wind was blowing. This indicates that the glasshouse was not adequately airtight as the levels at these points were about equal on a calm day.

The sampling system was used in other situations and the results (Table III) show that the highest CO₂ level was obtained in a crowded room (ballad session) while the lowest level was in an air conditioned conference room. The application to detect leakage of flue gases can only be used in a location where there are no people as the result would be influenced by CO₂ in the breath. Theoretically all the figures in Table 3 should be compared with an atmospheric level of 330 p.p.m. of CO₂. However,

in practice, it is unusual to find an empty room with CO₂ levels below 550 p.p.m. The term empty room in this context refers to a room in which there were people earlier in the day, or on the previous day.

Conclusion

The system described is simple and practical to operate and has many applications in agriculture and in air conditioning studies.

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Nitrogen and phosphorus determinations in animal feeds on a continuous flow system

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RECENT advances in the formulation of high performance animal feedstuffs have depended largely on the precise definition and control of nutrients. Two of the basic parameters are the levels of the ammonia and phosphates. Thus a precise knowledge of the status of these constituents, amongst others, in livestock rations is essential if optimum animal performance is to be achieved. By definition this statement calls for the calcium, phosphorus and nitrogen levels of raw materials of both vegetable and animal origin to be known to a similar precision.

The increase in workload as far as these analyses are concerned, is rising rapidly. Conventional manual methods to cope with the necessary throughputs would make heavy labour demands and no doubt would introduce an even higher total variability due to the large number of operators involved.

The content of this paper reports the application of the Cenco continuous flow analyzer to the simultaneous determination of total nitrogen and phosphorus in raw materials and formulated feedstuffs generally in use in the feed industry. The range of nitrogen as protein was between 4% and 70% and for phosphorus between 0.5 and 6%.

Apparatus

Continuous flow equipment supplied by Cenco, Breda, The Netherlands:

Transfer sampler
24 Channel pump
Heating bath
Two channel colorimeter
Two-pen potentiometric recorder
Electrically heated aluminium blocks, into which 60 holes 65 mm x 22 mm are drilled.

Reagents

Use analytical reagent grade unless otherwise stated.

Digestion reagents

- (a) Sulphuric acid.
(b) Digestion solution:
Take 200 cm³ concentrated sulphuric acid and add 200g of potassium sulphate and 0.75g selenium metal powder to it.

Digest for 5-6 hours until clear. Allow to cool and make up to 1 dm³ with concentrated sulphuric acid. Use 5 cm³ of the solution per 0.25g of sample.

- (c) Hydrogen peroxide, 30%.

Reagents for nitrogen determination

- (a) Sodium phenate: Dissolve 150 g phenol and 50 g sodium hydroxide in 1 dm³ distilled water.
(b) Sodium hypochlorite: Dilute 120 cm³ of a sodium hypochlorite (10-14% available chlorine) to 1 dm³ with distilled water.
(c) Sodium hydroxide solution: Dissolve 75 g of sodium hydroxide in 1 dm³ of distilled water.
(d) Brij solution: 0.1% in distilled water.
(e) Standard nitrogen reference solutions:
Stock solution: Accurately weigh 4.7150 g ammonium sulphate (vacuum oven dried at 70°C), dissolve in water, and dilute to 1 dm³. Solution contains 1 mg nitrogen/cm³ solution.
Working solution: See standard phosphorus reference solutions.

Reagents for phosphorus determination

- (a) Ammonium molybdate: Dissolve 7.5 g ammonium molybdate in 500 cm³ distilled water; carefully add 53 cm³ of concentrated sulphuric acid and dilute to 1 dm³ with distilled water.
(b) Reducing solution:
(1) Stock solution: Add 137 g NaHSO₃ and 5 g Na₂SO₃ to 800 cm³ of distilled water; heat to 50°C; add 2.5 g 1-amino-2-naphthol-4-sulphonic acid and stir to dissolve; filter and dilute to 1 dm³ with distilled water. Refrigerate this solution.
(2) Working solution: Dilute 100 cm³ of the stock solution to 1 dm³ with distilled water. Prepare fresh daily.
(c) Standard phosphorus reference solutions:
(1) Stock solution: Accurately weigh 4.3900 g potassium dihydrogen orthophosphate (vacuum-oven dried at 50°C), dissolve in water and dilute quantitatively to 1 dm³ with distilled water. Solution contains 1 mg P/cm³ solution.